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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C02F 1/70, A62D 3/00	A1	(11) International Publication Number: WO 97/14656 (43) International Publication Date: 24 April 1997 (24.04.97)
(21) International Application Number: PCT/CA96/00691 (22) International Filing Date: 18 October 1996 (18.10.96) (30) Priority Data: 9521293.2 18 October 1995 (18.10.95) GB (71) Applicant (for all designated States except US): UNIVERSITY OF WATERLOO [CA/CA]; Waterloo, Ontario N2L 3G1 (CA). (72) Inventors; and (75) Inventors/Applicants (for US only): GILLHAM, Robert, Winston [CA/CA]; 11 Crawford Street, Guelph, Ontario N1G 1Y9 (CA). ODZIEMKOWSKI, Marek, Szczepan [CA/CA]; 222 Gallamo Court, Kitchener, Ontario N2M 2Z5 (CA). O'HANNESIN, Stephanie, Frances [CA/CA]; 16 Carmine Place, Guelph, Ontario N1E 3V1 (CA). (74) Agent: ASQUITH, Anthony; 173 Westvale Drive, Waterloo, Ontario N2T 1B7 (CA).	(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: METHOD FOR TREATING CONTAMINATED WATER (57) Abstract <p>Groundwater, or other water contaminated with chlorinated organic contaminants, is passed through a permeable body of iron particles. The particles are coated with nickel, but the coating is incomplete, in that, in patches, the iron is directly exposed. The contaminants break down under prolonged proximity to the iron, the nickel enhancing the catalytic effect. The rate of breakdown is much faster than when bare iron particles were used. When the nickel is alloyed with phosphorus, or boron, even more rapid breakdown rates are achieved.</p>		

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Method for treating contaminated water

This invention relates to a development of the technology described in USA patent publication number US-5,266,213 (GILLHAM), published 13 June 1991.

Background to the Invention

In that technology, dissolved contaminants of the halogenated-organic type are broken down by passing the contaminated water over or through a body of iron granules, such as iron filings. Prolonged proximity to the iron, under strictly anoxic conditions, causes the breakdown reaction.

General Points of the Invention

It has now been found that coating the particles of iron with a small amount of nickel results in a great improvement in performance with respect to degradation rates of the contaminant. Also, it has been found, in cases where the degradation of the initial contaminant is to a substance that is also an halogenated organic contaminant, that such induced contaminants are less in concentration, and degrade comparatively much more quickly than they degrade when the particles are plain iron.

This new development, i.e coating the iron particles with nickel, gives degradation rates that can be almost an order of magnitude faster than when un-coated iron particles have been used.

It has also been found that, when the iron particles are coated with nickel, the need to exclude oxygen from the body of iron particles is not so dire. Therefore, surface water, industrial waste streams, etc, can be treated, in addition to oxygen-free groundwater.

Enhanced results have been encountered also when the iron particles are coated with an alloy of nickel-boron, or an alloy of nickel-phosphorus.

The manner in which the coating is applied is important. The coating should not be complete, i.e the coating should be patchy, whereby some of the surface of the iron is not coated. Thus, the water, and the contaminants in the water, are exposed to direct contact with the iron.

1 As regards the type of contaminant that can be treated, not only does the new
2 development apply to the treatment of the halogenated hydrocarbons, as with the original
3 technology, but it is also applicable for the treatment of contaminants of the kind that have
4 nitrogen groups in place of the halogens, for example.

5
6 As to the treatment material, other combinations of metals, i.e other than iron coated with
7 nickel, are contemplated. One of the key characteristics of the first metal, ie the metal that
8 constitutes the main weight of the treatment material, is that the first metal should be
9 cheap. Iron is good from this standpoint, of course, because of the ready availability of
10 cheap iron and steel scrap from industry. The second metal, ie the metal which is applied
11 as a patchy coating to the first metal particles, should be of a lower electro-chemical
12 activity than the first metal. Thus, nickel may be used as the second metal for coating iron
13 particles. On the other hand, zinc could not be used as the coating for iron particles.

14
15 One of the reasons the coating of the iron particles can be of the desired patchiness,
16 derives from the fact that the iron particles, being scrap from industrial processing, often
17 are rusty, i.e they have a coating of iron oxide. This oxide coating is itself uneven, both as
18 to thickness and as to chemical composition, and this unevenness is of assistance in
19 ensuring that the coating applied to the particles will be patchy.

20
21 The plating process tends to remove the oxide, and thus to leave bare the areas of the
22 surface of the particle that are un-coated. The bare metal thus exposed then tends not to
23 re-oxidise, because of the immediate proximity of the patches of the second metal, which
24 sets up an electro-chemical balance. A point to be noted is that if too much second metal
25 (nickel) is used in the coating, some of the nickel leaches out, which is itself a contaminant.
26 The desired small amount of nickel is instrumental in maintaining the electro-chemical
27 balance.

28
29 Preferably, in the invention, the coating process is electro-less, in that the coating is of the
30 kind that can be applied to the first metal without the input of electrical energy. An
31 electricity-applied plating process would be much more expensive.

32 33 List of Drawings

34
35 Fig 1 is a graph showing degradation of carbon tetrachloride (CT) over a period of time,
36 when the degradation results from contact with particulate iron;

37 Fig 2 is a graph showing the corresponding degradation of carbon tetrachloride over time,

1 when the degradation results from contact with particulate iron that has been coated with
2 nickel;

3 Fig 3 is a graph showing the corresponding degradation of carbon tetrachloride over time,
4 when the degradation results from contact with particulate iron that has been coated with a
5 nickel-phosphorus alloy, and with a nickel-boron alloy;

6 Fig 4 is a graph of another example of the kinds of degradation shown in Fig 3, the graph
7 being shown to a larger scale;

8 Fig 5 illustrates a treatment apparatus for treating in-ground groundwater, while the water
9 remains in its native aquifer;

10 Fig 6 illustrates a treatment apparatus for treating groundwater that has been removed from
11 its native aquifer;

12 Fig 7 illustrates a treatment apparatus for treating contaminated water in an effluent stream
13 from an industrial process.

14
15 Description of Preferred Embodiments, and of Experiments and Observations

16
17 The apparatuses and procedures depicted in the accompanying drawings and descriptions
18 are examples which embody the invention. It should be noted that the scope of the
19 invention is defined by the accompanying claims, and not necessarily by specific features of
20 exemplary embodiments.

21
22 Laboratory tests were conducted to examine the relative performance of nickel-coated iron
23 relative to the regular un-coated material for the reductive de-halogenation (breakdown) of
24 carbon tetrachloride in dilute aqueous solution. In the batch procedures the carbon
25 tetrachloride solution was added to hypo-vials with 10g of metal and the concentrations of
26 the parent and degradation products were monitored over time. Column experiments with
27 coated and uncoated iron were also performed using different flow rates.

28
29 Distribution of degradation products was dependent on residence time in the column.
30 Significant improvements on the degradation rates were observed using the Ni-Fe.
31 Complete disappearance of carbon tetrachloride, chloroform and dichloromethane was
32 achieved after a 3 hour residence time.

33
34 In the laboratory tests, a column containing particulate iron was provided: that is to say,
35 iron in the form of filings, powder, or granules, in which the metal is elemental iron (or
36 steel, with the usual steel constituent of a small percentage of alloyed carbon).

Water contaminated with carbon tetrachloride was fed into the column, and samples were drawn off at various times.

Fig 1 illustrates the expected rapid decline of the carbon tetrachloride -- expected, that is to say, from the teachings of the GILLHAM reference. However, as expected, the CT has degraded, not to harmless residues, such as methane and chloride, but to chloroform (TCM), which is also a contaminant. Also, one of the minor, but not negligible, substances resulting from the degradation of CT is the contaminant dichloromethane (DCM).

Thus, although passing water contaminated with carbon tetrachloride through a column of bare iron granules makes the CT disappear very quickly, the resulting products are themselves contaminants, and they degrade rather more slowly -- although they do eventually degrade more or less totally to harmless concentrations, and to harmless substances. Actually, the dichloromethane can be long-present, with plain iron.

The graph shown in Fig 2 illustrates the improvement that can arise when the iron particles are coated with nickel.

From Fig 2, it can be seen that the carbon tetrachloride degrades even faster than in Fig 1 (uncoated iron); also, the chloroform produced by the degradation of the CT is much less, and degrades faster; and finally the dichloromethane, although produced at first in larger quantities, declines at a measurably faster rate. Coating the iron particles with nickel therefore has a markedly beneficial effect on the totality of the degradation process.

The improvement caused by plating the particles with nickel may be illustrated also by the difference in half-life of the contaminants, when exposed to the iron, as shown in the following table.

Table 1: Normalised half lives of the chlorinated compounds resulting from carbon tetrachloride degradation (hr.m²/ml)

Substance	Fe/Ni Column	Fe column
Carbon tetrachloride	0.01	0.07
Chloroform (TCM)	0.04	3.85
Dichloromethane (DCM)	3.99	(no measurable degradation)

As far as degradation of the CT is concerned, it will be noted that a seven-fold improvement in half-life may be attributed to the step of coating the iron granules with

1 nickel. The TCM degradation is improved almost a hundred-fold. When the iron particles
2 are nickel-coated, the half-life of DCM becomes a significant 3.99 hr.m²/ml, rather than the
3 barely measurable rate found with bare iron.

4
5 Marked improvements in the treatment of other contaminant compounds are also observed:
6 for example, the breakdown rate of trichloro-ethene is improved about 20-fold when the
7 iron granules are coated with nickel.

8
9 It has been found that even greater improvements in degradation rates may be
10 accomplished when the iron particles are coated, not just with nickel, but with alloys of
11 nickel-boron, and of nickel-phosphorus.

12
13 Figs 3 and 4 illustrate this greater effect. Compared with the bare-iron rate of degradation,
14 the nickel-phosphorus rate is much faster. The nickel-boron rate is almost as fast as the
15 nickel-phosphorus rate. Both are faster still than the degradation rate of iron coated with
16 plain nickel.

17
18 The coating of the iron particles with nickel, and with the nickel-boron, and the nickel-
19 phosphorus alloys, was accomplished by immersing the iron particles in a bath containing a
20 suitable solution. In the bath, the iron particles were coated by means of electro-less (i.e
21 no electric current applied) plating.

22
23 Prior to immersing the iron particles in the bath, the particles were (partly) coated with
24 oxide. A reducing agent was introduced into the bath, and the composition of the reducing
25 agent determined whether the nickel in the coating was plain, or was alloyed with boron, or
26 phosphorus. The bath contained an acidic solution of nickel salts.

27
28 When the reducing agent was hydrazine N₂H₄ the coating was pure nickel; when the
29 reducing agent was dimethyl amino borate (CH₃)₂NH:BH₃ the coating was the alloy of nickel
30 and boron; when the reducing agent was sodium hypophosphite NaH₂PO₂ the coating was
31 the alloy of nickel and phosphorus.

32
33 There are other ways of activating the coating of the second metal to adhere to the
34 particles of the first metal, but the procedures as described require no input of electrical
35 energy, which is a great cost advantage.

36
37 The effect of the composition of the reducing agent and of the solution is illustrated in the

following table.

Table 2: Characteristics of the electro-less plating bath for Ni and Ni-alloys coating of Fe /Fe oxide catalyst support

(Data is given for the bath load of 1 kg of iron, per litre of plating solution)

<i>Reducing Agent Compound</i>	<i>Plating Bath Composition Solution</i>	<i>Concentration of solution grams/litre</i>	<i>Temp degC</i>	<i>Weight % of Ni</i>
1. (coating = nickel)				
N_2H_4		30		
	$NiCl_2 \cdot 6H_2O$	12	80	0.3 +/- 0.2
	$Na_2C_4O_6 \cdot H_2O$	7		
2. (coating = nickel-boron)				
$(CH_3)_2NH \cdot BH_3$		4.8		
	$NiCl_2 \cdot 6H_2O$	24	70	0.3
	$CH_3COONa \cdot 3H_2O$	18		
3. (coating = nickel-phosphorus)				
NaH_2PO_2		13 - 38		
	$NiCl_2 \cdot 6H_2O$	3 - > 12		
	H_3BO_3	7.5- 15	60	0.074 - > 0.3
	NaF	2.5 - 5		

The weights of the nickel deposited in the coatings, as a percentage of the weight of iron, are given in the above table.

In fact, the nickel-boron coating produced under the conditions of item 2 in Table 2 in fact is a triple alloy of nickel-boron-nitrogen. A simple double alloy of nickel-boron could be achieved if sodium boron hydrate were substituted.

A spot analysis was carried out, to ascertain the elements present in the coating at certain spots on the iron particles. This was an electron probe micro-analysis, performed using an electron beam of energy 20 keV. X-ray energy dispersion was measured at 0.1-0.6 keV and at 10 keV.

The results of this analysis, both for the nickel-phosphorus coating and for the nickel-boron

1 coating, made it clear that the nickel coating is not evenly distributed over the outer surface
2 of the iron particles. It is recognised that this is a key to the efficacy of the degradation
3 reaction. If the nickel were to completely cover the particles, the water (that is to say, the
4 contaminants in the water) would not be exposed directly to the iron. When the coating is
5 patchy, the enhanced-catalytic effect of the nickel can be realised, and yet the reaction is
6 not impeded by an insulating barrier of nickel.

7
8 Nickel-plating the particles by immersing them in a bath of nickel salts is one way of
9 realising the required patchy nature of the coating. Preferably, the particles should be
10 irregular in shape, since the irregular shape protects the coating in some places, while the
11 coating is rubbed off in other places. As explained in the GILLHAM reference, the source of
12 the iron particles generally will be the iron filings or other iron/steel debris from industrial
13 machining or fettling processes; therefore, inevitably the particles will be irregularly shaped,
14 but rather such particles are ragged and sharp-edged. Since the body of particles is to
15 comprise a permeable body, it is important that the size of the particles be such that a flow
16 of water can pass therebetween. Thus, the particles should not be dust-like, i.e so small
17 that the particles would settle, in use, whereby the body would lose permeability. On the
18 other hand, the particles should be small; the smaller the particle, the larger its area to
19 weight ratio, i.e the larger the surface area exposed to the water. A particle size of
20 between 1 milligram and 30 milligrams is preferred for the iron particles. Also, the iron
21 particles should be graded for size, i.e the particles making up the body should not differ in
22 size from each other to the extent that smaller particles would fill the interstices between
23 the larger particles, and thereby reduce permeability. Size grading where the weight of the
24 smallest particles is no less than about a tenth of the weight of the large particles, is
25 appropriate.

26
27 It may be noted that, in expressing the size of the particle as above, it is assumed that the
28 particle is solid metal, which is what is likely to be encountered in scrap metal. However,
29 if the metal is, for example, porous, whereby the particle has a quite different weight-to-
30 area ratio, the particle weight would be less.

31
32 Given that the nickel coating is patchy, and that the iron particles are irregularly-shaped,
33 and especially sharp-edged, and in the above size range, preferably the nickel coating on
34 the iron particle should weigh between about 0.01 percent and 5 percent of the weight of
35 the particle.

36
37 It has been mentioned that the nickel coating should be patchy, i.e that patches of the bare

1 iron should be exposed; but it is recognised that the coating does not need to be totally
2 absent in the bare patches. The coating may be characterised as patchy on the following
3 basis: first, an electron probe micro-analysis, using an electron beam of energy 20 keV, is
4 carried out at ten spots on the particle, to determine whether nickel is present at those
5 spots; if nickel is not detected at this energy level, the spot is deemed to be bare of nickel;
6 if nickel is detected at this energy level, the spot is deemed to be coated with nickel; of the
7 ten spots, between one and five should be bare of nickel, and between three and eight
8 should be coated with nickel.

9
10 The manner of applying the coatings, as described, gives rise to a coating that is even as to
11 its composition, where it is present. That is to say, where the coating is present, the
12 proportion of boron, or phosphorus, relative to the nickel, in the coating remains about the
13 same. For a given composition of the bath, the time the iron filings spend in the bath
14 determines the weight of the coating, and it is important that the temperature of the bath
15 be maintained. A typical time for the iron particles to spend in the plating bath is 1 or 2
16 hours.

17
18 It was noted that the fastest degradation rates came when the iron particles were coated
19 with the nickel-phosphorus alloy. In this case, phosphorus acts as a metal hydriding
20 process activator -- the effect being analogous to the known effect of alloying phosphorus
21 with palladium in some catalyst applications. The activator is called variously the promoter,
22 or transfer catalyst, by analogy. When adsorbed onto the metal surface, the transfer
23 catalyst activates co-adsorbed hydrogen to cross the barrier of metal-gas or metal-liquid
24 interface, and to become incorporated into the metal lattice to form a nickel hydride
25 hydrogenation catalyst.

26
27 It is understood that the plain nickel and the nickel-boron coatings are less effective than
28 the nickel-phosphorus coating, as regards the hydrogenation reaction, due to the absence
29 of an effective transfer catalyst. It may be noted that boron does not fall into the category
30 of a hydrogen-entry-promoter.

31
32 The effectiveness also of some rare earth intermetallic compounds is known, as a catalyst
33 for hydrogenation reactions. Their unusual effectiveness in breaking the hydrogen bond is
34 attributed to the high rate of hydrogen absorption.

35
36 The structures to be used for treating a real body of contaminated water are determined by
37 where the water is to be treated. If the water is treated in the ground, it is to be preferred

1 if the water, while remaining in the ground, can be caused to flow through an in-ground
2 body of the nickel-coated iron particles. Thus, if the ground is of such a nature as to permit
3 a flow of good velocity, and if the iron particles can be placed in a trench or other
4 receptacle in the path of the flowing contaminated water, that is generally the cheapest
5 clean-up solution.

6
7 Fig 5 illustrates a typical set-up. The plume 20 of contaminated water, in travelling through
8 the aquifer, passes through a trench 23, which has been excavated in the path of the
9 oncoming plume. The body of nickel-coated iron particles 25 is placed in the trench 23.

10
11 One of the benefits of keeping the water in the ground, i.e below ground, is that it is then
12 simple to keep oxygen away from the water; the presence of oxygen, or oxidising agents,
13 inhibits the breakdown reaction, even to the point of stopping the reaction.

14
15 Sometimes, however, it is cheaper to take contaminated groundwater out of the ground,
16 and convey the water into and through an above-ground vessel. The nickel-coated iron
17 particles are placed in the vessel, and the water passes through the particles. The treated
18 water may be used immediately, or the water may be discharged, after treatment, for
19 example into a river or stream.

20
21 Fig 6 illustrates a typical set-up. Groundwater is drawn out of a well 30, and pumped into
22 an above-ground vessel 32, which contains the body of nickel-coated iron particles 34.

23
24 It may be noted that the presence of the nickel coating increases the rate of the breakdown
25 reaction, to the extent that even if some oxidising agents might be present, yet still the
26 breakdown reaction will take place. Thus, the above-ground option was contra-indicated
27 (because of the need to exclude oxygen) in the case where the treatment material was
28 straight iron, as in the GILLHAM reference; but with the nickel-coated iron the above-
29 ground option is much more likely to be viable.

30
31 In cases where a cheap bulk filler material is required, which is inert with respect to the
32 breakdown reaction, generally sand is suitable. The grain sizes of the sand should be
33 compatible with the particle-sizes of metal, for avoidance of clogging.

34
35 Sometimes again, the water to be treated might be the effluent from an industrial process.
36 Fig 7 illustrates a typical set-up. The effluent is present in pipe 40, which discharges into
37 an above-ground vessel 43. In this case, the general rule would be that the effluent water

1 does contain oxygen, whereby the straight iron of GILLHAM would be quite unsuitable.

2

3 The need to exclude oxygen, and oxygen-supplying substances, arises because the
4 breakdown reaction does not start until the Eh voltage of the water has become negative.
5 However, when the iron particles are plated with nickel, the reaction can commence even
6 though the Eh probe may still be registering (slightly) positive voltages.

7

8 On the other hand, if oxygen is scrupulously excluded, it is likely that the residence time
9 needed to complete the breakdown reaction will in that case be shorter; that is to say, the
10 time the molecules of the contaminant need to spend in close proximity to the iron, is
11 shorter. In the case of the below-ground treatment, where oxygen is substantially
12 completely not present, and excluded, the residence time to break down the contaminants
13 would be at its shortest.

14

15 In a typical clean-up case, the prudent designer carries out a survey to determine the nature
16 and extent of the contaminant, its chemical composition and concentration, its velocity, the
17 permeability of the ground, and so on. Samples are taken, and experiments are conducted
18 in the laboratory, to determine the initial maximum concentration C . In a case where the
19 water has to be taken to drinking water standards, the safe level C_0 for that contaminant is
20 ascertained. Tests show the degradation rate at which that contaminant breaks down,
21 using the coated metal particles, as described. Degradation takes place exponentially,
22 whereby it is convenient to measure the rate in terms of half-life, HL, which is the time it
23 takes for the concentration level of that contaminant to be halved.

24

25 For example, a body of moving groundwater may contain a plume of TCE, having a
26 maximum concentration of 320 micrograms per litre of water. The drinking water limit for
27 TCE (in many jurisdictions) is 5 micrograms per litre. Experiments show that, with the
28 nickel-coated iron-particles available, the degradation half-life HL is, say, 2 minutes. In the
29 first two minutes, the concentration will drop to 160 micrograms per litre; then two
30 minutes after that to 80, then two minutes later to 40, then 20, then 10, then 5. Thus, a
31 total of six half-lives, or twelve minutes, should bring the concentration down to drinking
32 water standards.

33

34 The designer therefore should engineer the system to ensure that the water stays in
35 contact with the nickel-coated iron-particles for at least 12 minutes, plus whatever margin
36 of safety is deemed appropriate. The faster the velocity of the groundwater (often, there is
37 not much the engineer can do to change the velocity of the water), the longer he should

1 make the path through the body of particles, to achieve the required residence time.
2
3 It may be noted that, as mentioned in GILLHAM, metals other than iron can give rise to the
4 breakdown reaction. It has also been found that coating iron particles with a metal other
5 than nickel -- palladium, for instance -- gives beneficial results. However, providing a
6 palladium coating is much more expensive than providing a nickel, nickel-boron, or nickel-
7 phosphorus, coating.

Claims

- CLAIM 1.** Procedure for treating contaminated water, wherein:
the procedure includes the step of providing a body of particles of a first metal;
the procedure includes the step of applying a coating or layer of a second metal to
the particles of the first metal;
the coating or layer, thus applied to the particles of metal, is incomplete or patchy
with respect to the surface of the particle, in that at least a percentage of
the total surface area of the particle is un-coated;
the second metal is less electro-chemically active than the first metal;
the body of particles, thus provided, is of such consistency as to be permeable to
the passage of water therethrough;
the procedure includes the step of conducting a flow of the contaminated water
through the permeable body of particles;
and the procedure includes the step of maintaining the contaminated water in
contact with the particles for a sufficient residence time that chemical
breakdown of the contaminant occurs.
- CLAIM 2.** Procedure of claim 1, wherein the particles comprise iron or steel.
- CLAIM 3.** Procedure of claim 1, wherein the particles include an initial coating of
iron oxide.
- CLAIM 4.** Procedure of claim 2, wherein the particles are each of solid metal, and
have a weight of between 1 milli-gram and 30 milli-grams.
- CLAIM 5.** Procedure of claim 1, wherein the particles are of irregular shape.
- CLAIM 6.** Procedure of claim 2, wherein the particles of iron are mixed with
particles of another substance, such as sand, which is inert with respect to
the breakdown reaction.
- CLAIM 7.** Procedure of claim 1, wherein the coating includes nickel.
- CLAIM 8.** Procedure of claim 7, wherein the coating consists of substantially pure

nickel.

CLAIM 9. Procedure of claim 7, wherein the coating comprises an alloy of nickel and a non-metal.

CLAIM 10. Procedure of claim 7, wherein the coating comprises an alloy of nickel-boron.

CLAIM 11. Procedure of claim 7, wherein the coating comprises an alloy of nickel-phosphorus.

CLAIM 12. Procedure of claim 7, wherein the coating comprises an alloy of nickel-boron-nitrogen.

CLAIM 13. Procedure of claim 2, wherein the coating includes nickel and the procedure includes the step of so applying the coating that the weight of the coating is more than 0.01 percent, and less than 5 percent, of the weight of the particle.

CLAIM 14. Procedure of claim 13, wherein the percentage of the surface area of the coating to the total surface area of the particle is at least ten percent.

CLAIM 15. Procedure of claim 13, wherein the percentage of the surface area of the coating to the total surface area of the particle is at most ninety-five percent.

CLAIM 16. Procedure of claim 13, wherein the percentage of the surface area of the coating to the total surface area of the particle is between fifty percent and seventy-five percent.

CLAIM 17. Procedure of claim 1, wherein the contaminant is a halogenated hydrocarbon.

CLAIM 18. Procedure of claim 1, wherein the contaminant is a nitrogenated

hydrocarbon.

CLAIM 19. Procedure of claim 1, wherein:

the contaminant is of the type that is a contaminant even though present in the water only in tiny traces;

whereby breakdown substances accumulate in, and are present in, such small quantities as to leave the body of particles permeable;

and the breakdown substances are of the kind that are non-contaminating in the tiny trace quantities.

CLAIM 20. Procedure of claim 1, wherein the contaminant is present in the water in bulk quantities.

CLAIM 21: Procedure of claim 1, wherein the breakdown substances are non-solid.

CLAIM 22. Procedure of claim 1, wherein the procedure includes the step of conveying the contaminated water through the permeable body of metal particles.

CLAIM 23. Procedure of claim 22, wherein the contaminated water is groundwater in its native aquifer, having a velocity therethrough, and the step of conveying the water through the permeable body of metal particles comprises placing the body of particles in the ground, in the path of the moving groundwater.

CLAIM 24. Procedure of claim 22, wherein the procedure includes the step of conveying the contaminated water into and through a vessel, above ground, and the step of conveying the water through the permeable body of metal particles comprises placing the body in the vessel.

CLAIM 25. Procedure of claim 22, wherein the contaminated water is an effluent stream from an industrial process, which is conveyed into and through a vessel, and the step of conveying the water through the permeable body of iron particles comprises placing the body in the vessel.

CLAIM 26. Procedure of claim 1, wherein the procedure includes substantially excluding oxygen and oxygen-supplying substances, from the water, and from the body of metal particles.

CLAIM 27. Procedure of claim 1, wherein the breakdown of the contaminant is into chemical substances of such low toxicity as to be safe at the concentrations produced.

CLAIM 28. Procedure of claim 1, wherein:

the procedure includes the step of carrying out a survey and making a preliminary determination that the contaminant is one that can be broken down by prolonged proximity with a metal;

the procedure includes the step of providing the body of metal particles in sufficient quantity, and conducting contaminated water through at such a flow rate, as to cause the concentration of the contaminant to drop to a predetermined safe level of the contaminant.

CLAIM 29. Procedure of claim 28, wherein:

the step of carrying out the survey includes the steps of carrying out measurements to determine the concentration C of the contaminant in the water, of noting the predetermined safe level of concentration C_0 of that contaminant, of carrying out measurements to determine the half-life HL of that contaminant when placed in close proximity to the coated particles;

the steps of providing the body of metal particles, and of conducting the water therethrough at such a flow rate, are such as to cause the contaminants in the water to have a residence time RT in close proximity to the particles, where RT is a sufficient number of multiples of HL as to cause the concentration to drop from C to C_0 .

CLAIM 30. Procedure of claim 1, wherein the step of applying the coating includes the step of immersing the particles of metal in an electro-less bath containing salts of the substance which is to be coated onto the particles.

CLAIM 31. Procedure of claim 30, where the salts include $NiCl_2 \cdot 6H_2O$.

CLAIM 32. Procedure of claim 30, where the salts include $\text{Na}_2\text{C}_4\text{O}_6 \cdot \text{H}_2\text{O}$.

CLAIM 33. Procedure of claim 30, where the salts include $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$.

CLAIM 34. Procedure of claim 30, where the salts include $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$.

CLAIM 35. Procedure of claim 30, where the salts include $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$.

CLAIM 36. Procedure of claim 30, where the salts include H_3BO_3 .

CLAIM 37. Procedure of claim 30, where the salts include NaF.

CLAIM 38. Procedure of claim 30, wherein the bath also contains a reducing agent.

CLAIM 39. Procedure of claim 38, wherein the reducing agent is hydrazine.

CLAIM 40. Procedure of claim 38, wherein the reducing agent is dimethyl amino borate.

CLAIM 41. Procedure of claim 38, wherein the reducing agent is sodium hypophosphite.

CLAIM 42. Procedure of claim 38, wherein the reducing agent is sodium-boron hydrate.

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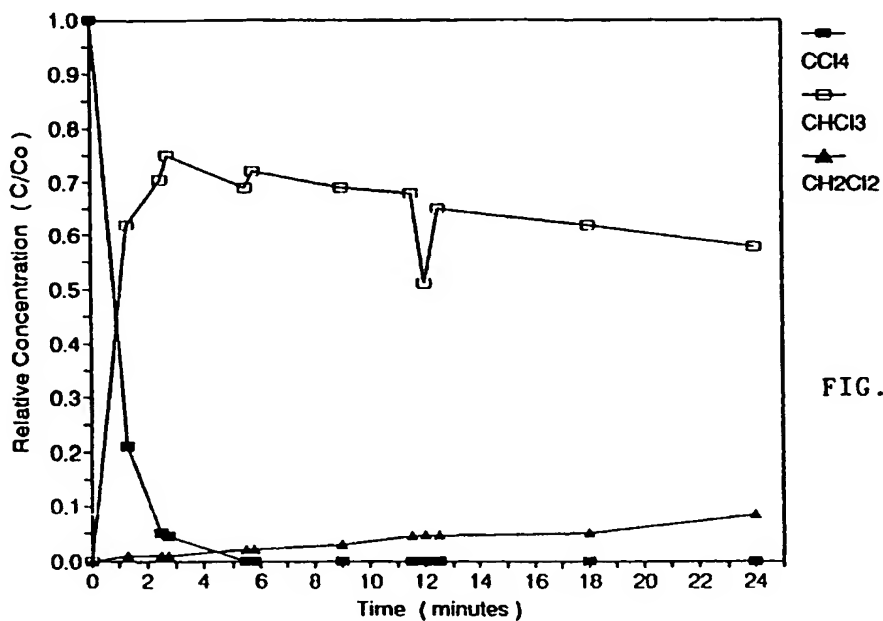


FIG. 1

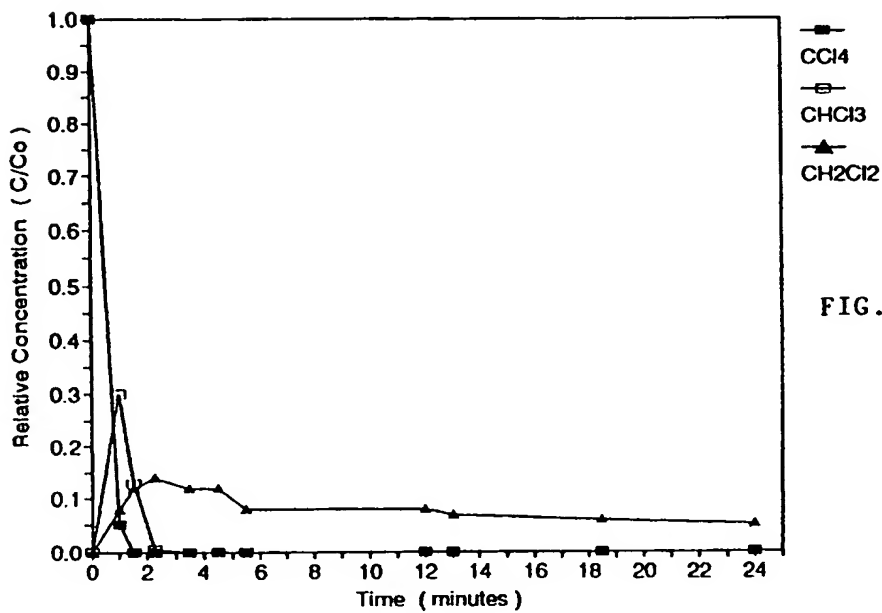


FIG. 2

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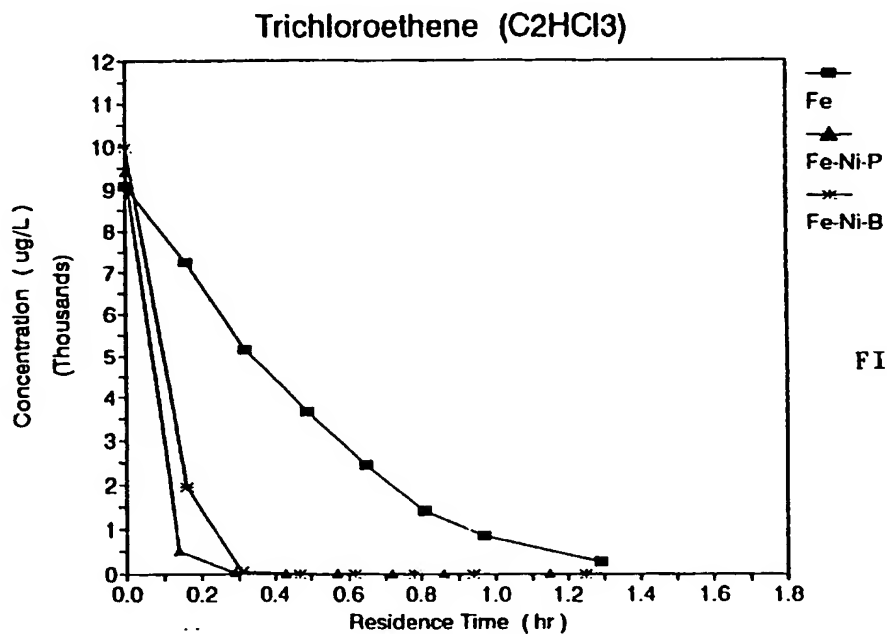


FIG. 3

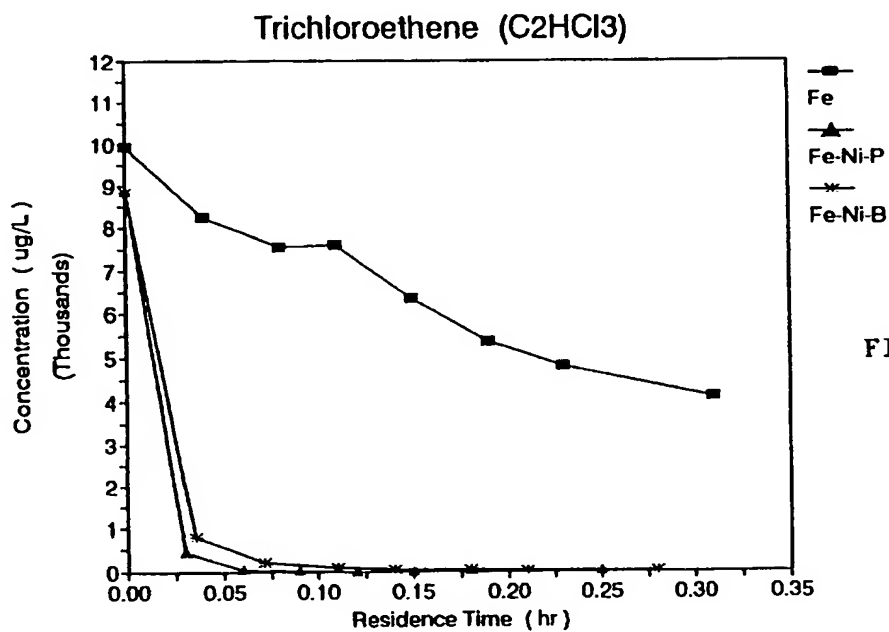


FIG. 4

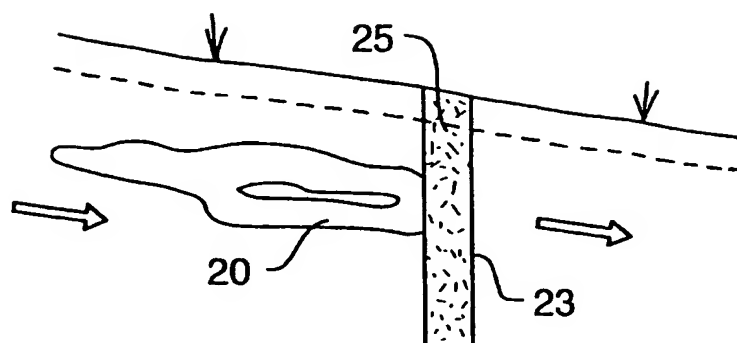


FIG. 5

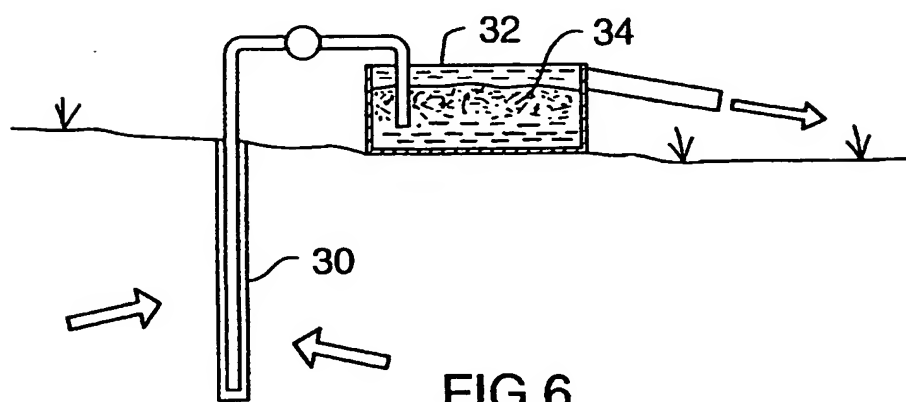


FIG. 6

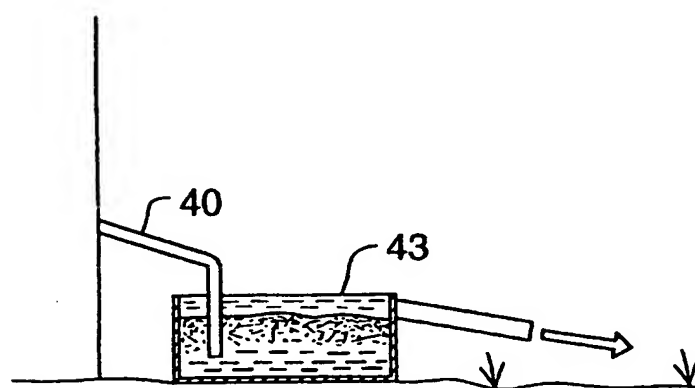


FIG. 7

INTERNATIONAL SEARCH REPORT

International application No.

PC. JA 96/00691

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C02F 1/70, A62D 3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: A62D, C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DIALOG: ALLSCIENCE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO, A1, 9620137 (RESEARCH CORPORATION TECHNOLOGIES, INC.), 4 July 1996 (04.07.96), page 31, figure 10, claims 1,6, abstract	1-2,7-8, 19-24,30-31, 33,35
X	US, A, 4219419 (KEITH H. SWEENEY), 26 August 1980 (26.08.80), column 6, line 17 - line 31; column 10, line 8, claims 1,10	1-2,7-8, 17-28
Y		6,30-31,33, 35,38,41
Y	EP, A1, 0387816 (WELLA AKTIENGESELLSCHAFT), 19 Sept 1990 (19.09.90), column 2, line 46 - line 49; column 7, line 33 - line 36, figure 5, claim 1	1

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

26 February 1997

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Date of mailing of the international search report

18.03.97

Authorized officer

Bo Bergström

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA 96/00691

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	US, A, 3255033 (A.F. SCHMECKENBECHER), 7 June 1966 (07.06.66), claim 1 —	30-31, 33, 35, 38, 41
A	GB, A, 2255087 (ROBERT WINSTON GILLHAM), 28 October 1992 (28.10.92), page 12, line 24 - page 13, line 5 — -----	1

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International application No.

PCT/CA 96/00691

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			US-A-	4382865	10/05/83
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			DE-U-	9002872	09/08/90
			DE-D-	59002686	00/00/00
US-A-	4382865	10/05/83	EP-A-	0012162	25/06/80
			US-A-	4219419	26/08/80
US-A-	3255033	07/06/66	NONE		
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			AU-A-	1982892	21/12/92
			CA-A-	2108982	12/11/92
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			JP-T-	6506631	28/07/94
			US-A-	5534154	09/07/96
			WO-A-	9219556	12/11/92